RELATING OCEAN OPTICS TO PHOTOCHEMICAL TRANSFORMATIONS OF DISSOLVED ORGANIC CARBON IN COASTAL WATERS

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LONG-TERM GOAL

The long-term goal of this research is to use remotely sensed ocean optical data to estimate the regional and global scale significance of photochemistry to dissolved organic carbon (DOC) cycles in the ocean.

SCIENTIFIC OBJECTIVES

The central objective of this research program is to examine quantitatively the links between optical measurements and photochemical carbon transformations in the sea. Our goal is to establish quantitative methods to relate variability in water-leaving radiance to photochemical reactions which lead to loss of dissolved organic matter (DOM) in the photic zone. In the examination of these quantitative relationships, we also hope to gain an understanding of both the dominant variables controlling UV optics in the mixed layer and the critical parameters influencing DOC photochemical reactions in seawater.

APPROACH

To achieve the objectives stated above requires a wavelength dependent description of the <u>in situ</u> optical field for ultraviolet radiation (UV) together with spectral efficiency data for photooxidation of DOM. Our general approach uses three connected principles:

(1) Diffuse attenuation coefficients for visible spectral irradiance can be related to ocean color (i.e., ratios of near-surface water-leaving radiance; Austin and Petzold 1981). Preliminary results indicate that comparable relationships between water-leaving radiance and diffuse attenuation of UV radiation can also be determined (see Figure 1).
(2) Colored dissolved organic matter (CDOM) is a dominant contributor to the absorption and attenuation of UV in coastal waters. With appropriate caution, and proper accounting for adsorption by particulates, diffuse attenuation of UV can be related directly to absorption by dissolved organic matter.
(3) The absorption of UV by CDOM leads to photochemical transformations that include the destruction of chromophores and the production of lower-molecular weight compounds. Wavelength-dependent quantum yields for these transformations can be determined experimentally as action spectra.

Given measurements of solar radiation and upwelling radiance at the sea-surface, we will estimate photochemical transformations of surface-layer DOM by applying empirical relationships between: (1)

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reflectance and diffuse attenuation, (2) spectral diffuse attenuation and UV absorbance, and (3) UV absorbance and action spectra for photochemical transformations.

Field optical data are collected with two instruments (Satlantic, Inc.) that add UV measurements to visible wavebands compatible with the SeaWiFS ocean color satellite. The first is a modified Tethered Spectral Radiometer Buoy (TSRB-II) which simultaneously measures incident irradiance (Ed) and upwelling radiance (Lu) in 14 wavebands, including 4 in the UV (2 nm bandwidth). The second is a SeaWiFS Profiling Multichannel Radiometer (SPMR) which measures vertical profiles of downwelling irradiance in wavebands identical to the TSRB-II. Both instruments are deployed simultaneously to accumulate UV/VIS optical data (Ed, Lu, & Kd) while collecting discrete rosette samples at the same station. Each sample is evaluated for particulate absorption (including detrital correction), dissolved absorption (at least in the UV), and particulate pigments.

We use two laboratory irradiation strategies to quantify photochemical carbon mineralization (DIC & CO): (1) Full spectrum irradiations with a solar simulator (DSET Suntest CPS, Heureus) and/or natural sunlight that allow evaluation of the statistical uncertainties and upper bounds for mathematical predictions of photoproduction in different waters. (2) Narrow bandwidth monochromatic irradiations (normally using an Oriel 1/4 meter monochromator with 1000W Xe source) that establish wavelength-based quantum efficiencies (Φ) for photochemical and coincident physical/chemical (ex. fading) alterations of the DOM . Photochemical production rates are compared to wavelength dependent extinction coefficients, irradiation history, bleaching rate, and environmental variables (pH, temperature, salinity, etc.). The combination of spectral photochemical efficiency data, absorbance data, irradiation profiles generated either using the SPMR or optical models, and measurements of solar spectral irradiance will allow predictions of whole column photoproduction.

Using relationships developed by deployments of the TSRB-II and SPMR, we plan to combine remotely-sensed data with irradiance and water optical models to estimate the photomineralization of DOM in the coastal ocean (á la. J.J. Cullen et al., ASLO 1997). These data will represent the beginning of regional photochemical inventories and a starting point for long term regional scale studies of photochemical carbon transformations in the coastal ocean.

S. Johannessen (PhD. student) and W. Miller (PI) are involved in all components of this approach. The field optical component benefits greatly from the participation of J.J. Cullen (w/ R. Davis, B. Nieke, A. Ciotti, and Satlantic, Inc.: instrument development, optical expertise, field and computer assistance) and collaboration with N. Blough (w/ A. Vodacek, F. Hoge: additional optical data, shared shiptime).

WORK COMPLETED

We have developed the 14-channel UV-vis reflectance radiometer buoy (the TSRB-II Lu sensors ride high, eliminating the need to propagate data to the surface) and improved procedures for calculating Kd and dark-correction (collaboration with M. Lewis and J. Cullen). The SPMR has been deployed to test design refinements that include alternative cosine collector materials and the addition of a WETStar miniature fluorometer for simultaneous chlorophyll fluorescence profiles.

The TSRB-II and SPMR have measured UV and visible reflectance and diffuse attenuation during four cruises in 1997: two cruises in the Atlantic Bight with complete transects of the Delaware and Chesapeake Bays (collaboration with N. Blough, Univ. Maryland), one cruise in the St. Lawrence estuary and Gulf of St. Lawrence, and one cruise to the Bering Sea in June 1997 (collaboration with J. Cullen, participation of my ONR funded graduate student, Sophia Johannessen). These results will be used to

develop photochemical and mathematical relationships for the estimation of photochemical fluxes from remotely sensed data in diverse water types.

New MATLAB® code has been developed to speed the analysis of both field and laboratory spectral data.

We have designed, constructed and begun to optimize and calibrate an irradiation box (15 long-pass filters over custom quartz containers) which will allow quantum yield data to be generated more quickly than traditional monochromatic irradiation techniques, possibly eliminating the need for sample storage.

RESULTS

We have accumulated discrete samples and UV/VIS optical data (Ed, Lu, & Kd) for waters of various sea state ranging from 0 to 36 ppt salinity in sky conditions ranging from heavy overcast to bright sun. Successful deployment of these new optical packages and the acquisition of quality data during the first years of this grant represent a significant technical accomplishment. On each cruise, discrete water samples were also collected for evaluation of particulate and dissolved absorbance and for photochemical characterization. Based on data from the Atlantic Bight (Figure 1, J.J. Cullen et al., ASLO 1997) and the Gulf of St. Lawrence (Nieke et al., AGU 1998)., our initial approach to develop quantitative relationships between visible reflectance and Kd's for the UV looks very promising.

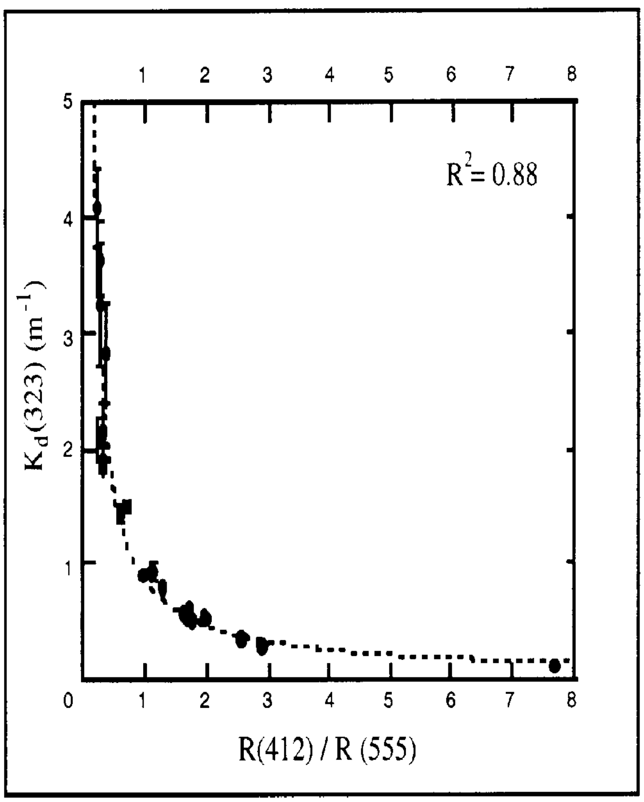

Figure 1. Relationship between visible reflectance and Kd in the UV. *RV Cape Henlopen* data.

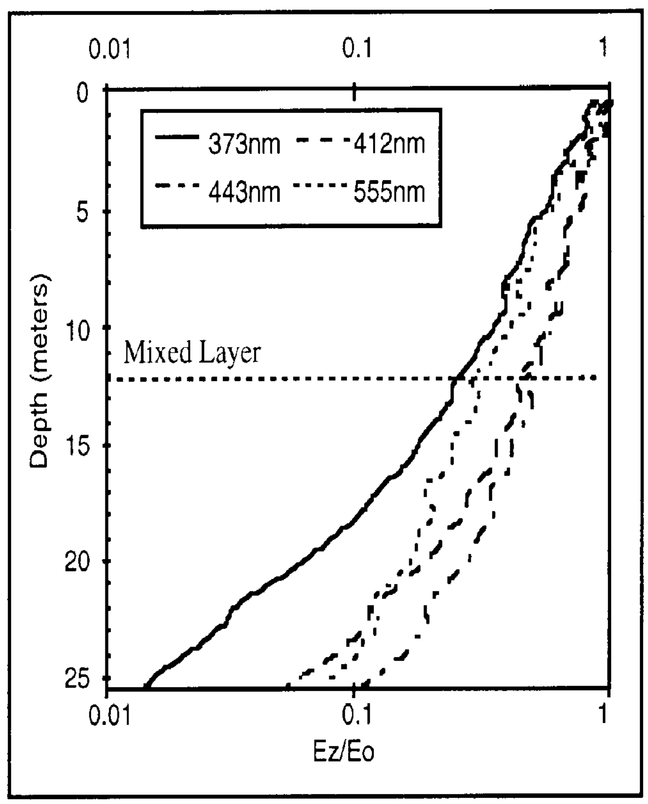

Figure 2. Irradiance ratio profiles for selected UV and visible wavebands. *RV Cape Henlopen* data.

Vertical optical profiles of seasonally stratified water in August supported the hypothesis that photochemical fading of CDOM is a significant process affecting optical properties in the mixed layer. At these stations, an increase in UV attenuation was observed at the base of the mixed layer while an equivalent trend was not seen for visible wavelengths (Figure 2, note 373 vs. 555 nm and 412 vs. 443 nm; presented by W. Miller et al., ASLO 1997). This optical data, used with concurrent salinity profiles, is consistent with the presence of a photochemically faded surface layer. At most other coastal stations, the UV signal was attenuated to below detection before reaching the mixed layer depth, supporting the use of mixed layer Kd in the photochemical calculations for whole water column production. In both cases, good definition of Kd's for UV in the mixed layer were obtained for use in relating to the visible reflectance. These preliminary data are very promising and indicate the general utility of these instruments in the field study of CDOM photochemistry and its relation to observed optical properties.

IMPACT / APPLICATION

The optical properties of CDOM in the ocean control photochemical rates and influence the interpretation of ocean color. Based on preliminary data from our first field season, we feel that instrumentation capable of characterizing UV radiation in the surface ocean will prove invaluable to the understanding of the variability in the CDOM signal. While a large effort will be needed on both optical and photochemical research fronts, the approach developed thus far (á la J.J. Cullen et al., ASLO 1997) appears to be sound and should lead to novel and critical insight on the link between ocean optics and photochemical carbon transformations.

TRANSITIONS

In addition to our main work in the Atlantic Bight, both instruments developed as part of this project have also been successfully deployed in the Gulf of St. Lawrence (B. Nieke, post. doc. w/ Cullen, Dalhousie Univ.) and the Bering Sea (Cullen). The TSRB-II (mounted in a modified frame for very shallow Lu deployment) has been deployed to study UV effects on coastal lakes (collaboration with J. Cullen, and T. Clair, Environment Canada). Parts of the field data for the Atlantic Bight will be prepared for publication with N. Blough (Univ. Maryland, ONR funded). Our field optical data is being used as part of a larger data set (M. Lewis, Dalhousie Univ., ONR) for development of MATLAB® algorithms for optical data base management. Currently, the photochemical data is not ready for transition.

RELATED PROJECTS

As stated above, we have collaborated with N. Blough (ONR) on field work, sharing optical data and ship time. His efforts are on CDOM photochemistry.

We have a collaborated with M. Lewis (ONR), also at Dalhousie, in his study of bio-optical variability and development of novel optical instrumentation. J. Cullen works closely with both Dr. Lewis and myself on optical models, data analysis, and instrument development. The timely development of our novel Satlantic instruments depends heavily on this relationship.
A new project was started in 1997, funded by the Canadian National Science and Engineering Council (NSERC), to study DOM photochemistry in a Arctic polynya. A postdoc, a masters student, and I will

use photochemical approaches similar to those developed for my ONR project. We are not funded for optical measurements in this project.

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